metal-organic compounds

Acta Crystallographica Section C Crystal Structure Communications ISSN 0108-2701

3-Methylamido-3',4'-ethylenedithiotetrathiafulvalene(+) potassium tetraisothiocyanatomercury(II)

Sergey Simonov,^a* Leokadiya Zorina,^a Natal'ya Kushch,^b Cécile Mézière^c and Patrick Batail^c

^aInstitute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, MD, Russian Federation, ^bInstitute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, MD, Russian Federation, and ^cChimie, Ingénierie Moléculaire et Matériaux d'Angers (CIMMA), UFR Sciences – Bât. K, 2 Bd Lavoisier, 49045 Angers, France Correspondence e-mail: simonovsv@rambler.ru

Received 19 December 2006 Accepted 5 February 2007 Online 28 February 2007

In the title compound, $(C_{10}H_9NOS_6)K[Hg(SCN)_4]$ or $(EDT-TTF-CONHMe)K[Hg(SCN)_4)]$, fully oxidized organic $(EDT-TTF-CONHMe)^+$ radical cations form quasi-one-dimensional stacks running along the monoclinic 2_1 axis and alternating along the crystallographic [101] direction with inorganic anion stacks made from mixed $K^+-[Hg(SCN)_4]^{2-}$ ribbons. For each anion, three essentially collinear SCN ligands interact with the K^+ ions *via* short $N \cdots K$ contacts, while the terminal N atom of the fourth SCN group is engaged in a number of hydrogenbond contacts with the -CH, -NH and $-CH_2$ hydrogen-bond donors of the amide function. Radical cations are dimerized along the stacks and the crystal conductivity is activated.

Comment

3-Methylamido-3',4'-ethylenedithiotetrathiafulvalene (EDT– TTF–CONHMe; Heuzé *et al.*, 1999) is one of a series of π donor molecules whose hydrogen-bond donor/acceptor group acts in the solid state as a structure-directing functionality, eventually enhanced upon redox activation (Fourmigué &



Batail, 2004), as illustrated by several recent examples (Heuzé *et al.*, 2000, 2003; Baudron *et al.*, 2003). The $[Hg(SCN)_4]^{2-}$ anion was selected to be used in the title compound, (I), because of its versatile conformation in addition to a noted ability to form metallic and superconducting radical cation salts with a variety of organic donors.

As shown in Fig. 1, radical cation stacks and chains of anionic motifs are segregated and run along the monoclinic 2_1 axis. The labeled molecules with displacement ellipsoids are shown in Figs. 2 (organic donor) and 3(b) (anion), respectively. There is one independent radical cation located in a general position. The central C1==C2 bond length [1.391 (5) Å] of the TTF fragment is the most sensitive to the degree of charge transfer, or net π -donor oxidation state, and is characteristic of a fully oxidized (*viz*. 1+) donor molecule. A zigzag mode of intermolecular overlap with two different patterns of overlap is observed, indicating that the stack is dimerized (Fig. 2). Intradimer overlap pattern A involves a strong intradimer interaction with short S \cdots S, S \cdots C and C \cdots C van der Waals



Figure 1 The crystal structure of (I).



Figure 2

(a) Intra-dimer (pattern A) and (b) inter-dimer (pattern B) overlap between the radical cations along the stack. Displacement ellipsoids are drawn at the 50% probability level.





(a) The donor-donor (dashed lines) and donor-anion (dotted lines) interactions. (b) The anion ribbon stabilized by $N \cdots K$ contacts. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) -x + 2, -y + 1, -z + 1; (ii) -x + 2, -y + 2, -z + 1; (iv) x + 1, y + 1, z; (v) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (vi) x, y + 1, z.]

contacts [see Table 1 and Fig. 3(a)], while only one $S3 \cdots S3$ contact for interdimer interaction pattern *B* is observed. The intra- and inter-dimer interplanar separations within the stack, calculated using the central six atoms of the TTF fragment, are 3.355 (8) and 3.460 (8) Å, respectively.

The complex anion $K^+[Hg(SCN)_4]^{2-}$ is located in a general position near the twofold screw axis 2₁. The Hg atom adopts a tetrahedral coordination involving S atoms, yet each of the SCN ligands adjusts to the crystal environment by rotating around the Hg-S bonds. Note that the conformation of the anion revealed in (I) has not been reported previously. Analysis of structures collected in the Cambridge Structural Database (Bruno *et al.*, 2002; Allen, 2002) indicates that, in the previously reported structures, at most two SCN vectors of the $[Hg(SCN)_4]^{2-}$ anion appear to be near collinear instead of three as in the present compound. These three ligands interact with the K⁺ ion *via* short N···K contacts of 2.780 (4)–3.108 (4) Å, stabilizing the anion ribbon as shown in Fig. 3(*b*). The fourth SCN ligand protrudes out towards the donor

molecules, its terminal N2A atom being involved in a number of hydrogen-bond contacts with the amide groups (Fig. 3*a* and Table 2). The recurrent tweezer-like hydrogen-bonded sevenmembered ring motif (Heuzé *et al.*, 2000; Fourmigué & Batail, 2004) acting upon the combined effect of activated –NH and $-Csp^2$ H hydrogen-bond donors is again identified here. In addition, the radical cation stacks are connected to adjacent anion ribbons by short O···K [2.606 (3) Å] and S···S contacts along [101]. The coordination polyhedron around the K⁺ cation is a distorted octahedron composed of one O and five N atoms; this differs from the eight- (4N + 4S) and seven-coordination (4N + 3S) of K in α - and δ -(BEDT-TTF)₂K[Hg-(SCN)₄], respectively (Oshima *et al.*, 1989; Kazheva *et al.*, 2002). The crystals of (I) are semiconducting, as expected for a dimerized stack.

Experimental

Single crystals of (I) were obtained by electrooxidation, at constant current ($I = 2 \mu A$) and 293 K, of EDT–TTF–CONHMe in 1,1,2-trichloroethane solution containing 10% (ν/ν) dried ethanol. Plate-like crystals grew on the anode after three weeks.

Crystal data

V = 2649.2 (6) Å ³
Z = 4 Mo K α radiation μ = 6.78 mm ⁻¹ T = 294 (2) K 0.15 × 0.06 × 0.02 mm
25746 measured reflections 6827 independent reflections 4594 reflections with $I > 2\sigma(I)$ $R_{int} = 0.040$
309 parameters H-atom parameters constrained $\Delta \rho_{max} = 0.88 \text{ e} \text{ Å}^{-3}$ $\Delta \rho_{min} = -0.61 \text{ e} \text{ Å}^{-3}$

Table 1

Intermolecular contacts (Å) in the donor stack.

$S1 \cdot \cdot \cdot S4^i$	3.384 (1)	$C1 \cdot \cdot \cdot C1^i$	3.577 (7)
$S2 \cdot \cdot \cdot S3^{i}$	3.350(1)	$C4 \cdot \cdot \cdot C5^i$	3.394 (5)
$S3 \cdot \cdot \cdot S3^{ii}$	3.574 (2)	$C1 \cdot \cdot \cdot C2^i$	3.363 (5)
S3···C4 ⁱ	3.620 (3)	$C3 \cdot \cdot \cdot C6^i$	3.442 (5)
S5···C9 ⁱ	3.543 (4)	$C3 \cdot \cdot \cdot C5^i$	3.564 (5)

Symmetry codes: (i) -x + 2, -y + 1, -z + 1; (ii) -x + 2, -y + 2, -z + 1.

Table 2			
Hydrogen-bond	geometry	(Å,	°).

$D-\mathrm{H}\cdots A$	D-H	$H \cdots A$	$D \cdots A$	$D - H \cdots A$
$C7A - H7C \cdot \cdot \cdot N1^{i}$	0.97	2.63	3.45 (2)	142
$C8-H8B\cdots N2A^{iii}$	0.97	2.71	3.539 (9)	144
$N1-H1\cdots N2A^{iv}$	0.86	2.10	2.938 (5)	165
$C5-H5\cdots N2A^{iv}$	0.93	2.41	3.298 (5)	160

Symmetry codes: (i) -x + 2, -y + 1, -z + 1; (iii) -x + 1, -y, -z + 1; (iv) x + 1, y + 1, z.

The final refinement was carried out in the space group $P2_1/n$, chosen on the basis of the systematic absences and successful refinement of the structure. The positions of the methyl and ethylene H atoms were calculated as riding, in accordance with the HFIX 137 and HFIX 23 instructions of *SHELXL97* (Sheldrick, 1997), with $U_{iso}(H)$ values of 1.5 and 1.2 times $U_{eq}(C)$, respectively. The H atoms of $-Csp^2H$ and -NH groups were located in difference electrondensity syntheses and constrained by an AFIX 43 instruction $[U_{iso}(H) = 1.2U_{eq}(C,N)]$. The terminal ethylene group of the radical cation is disordered over two positions in an approximate 3:1 ratio and C-C distances were restrained to be equal.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2* and *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank R. P. Shibaeva for fruitful discussions and L. I. Buravov for the resistance measurements. This work was supported by the Russian Foundation for Basic Research (project No. 05-02-16980) and INTAS (project No. 04-83-4001). Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3066). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). Acta Cryst. B58, 380-388.
- Baudron, S. A., Batail, P., Rovira, C., Canadell, E. & Clérac, R. (2003). Chem. Commun. pp. 1820–1821.
- Bruker (2005). APEX2. Version 1.27. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). Acta Cryst. B58, 389–397.
- Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.
- Farrugia, L. J. (1999). J. Appl. Cryst. 32, 837-838.
- Fourmigué, M. & Batail, P. (2004). Chem. Rev. 104, 5379-5418.
- Heuzé, K., Fourmigué, M. & Batail, P. (1999). J. Mater. Chem. 9, 2373–2379. Heuzé, K., Fourmigué, M., Batail, P., Coulon, C., Clérac, R., Canadell, E.,
- Auban-Senzier, P., Ravy, S. & Jerome, D. (2003). Adv. Mater. 15, 1251–1254. Heuzé, K., Mézière, C., Fourmigué, M., Batail, P., Coulon, C., Canadell, E.,
- Auban-Senzier, P. & Jérome, D. (2000). *Chem. Mater.* **12**, 1898–1904. Kazheva, O. N., Canadell, E., Aleksandrov, G. G., Kushch, N. D. & Dyachenko,
- O. A. (2002). Acta Cryst. B58, 471–476.Oshima, M., Mori, H., Saito, G. & Oshima, K. (1989). Chem. Lett. pp. 1159– 1162.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.